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Benzyl 2-Acetamido-4-azido-3-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-2,4-dideoxy- β -D-glucopyranoside

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Abstract

The title compound, C₃₈H₄₂N₄O₆Si, is a key intermediate in the preparation of inhibitors for bovine β -1,4-galactosyl transferase. The configuration of the sugar was as expected. Libration of the *tert*-butyldiphenylsilyl group about an axis normal to the glucose ring is not coupled to the glucose. Intermolecular hydrogen bonding at the acetamido group leads to a sixfold screw axis.

Comment

During a recent study of inhibitors of bovine β -1,4-galactosyl transferase, acceptor analogues were prepared by a sequence of reactions starting from benzyl *N*-acetyl- β -D-galactosaminide. The title compound, (I), is a key intermediate in this sequence, representing the stage at which the configuration is reversed to give the required glucosaminide products (Field, Neville, Smith & Ferguson, 1994). The stereochemistry was found to be as expected, confirming the validity of the reaction sequence.

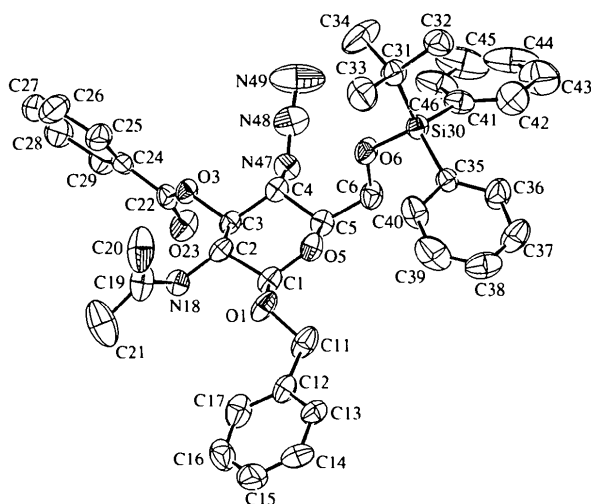
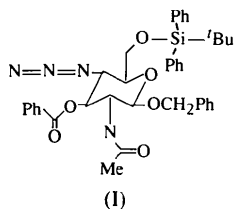


Fig. 1. Displacement ellipsoid plot (50% probability) of benzyl 2-acetamido-4-azido-3-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-2,4-dideoxy- β -D-glucopyranoside perpendicular to the glucose ring.

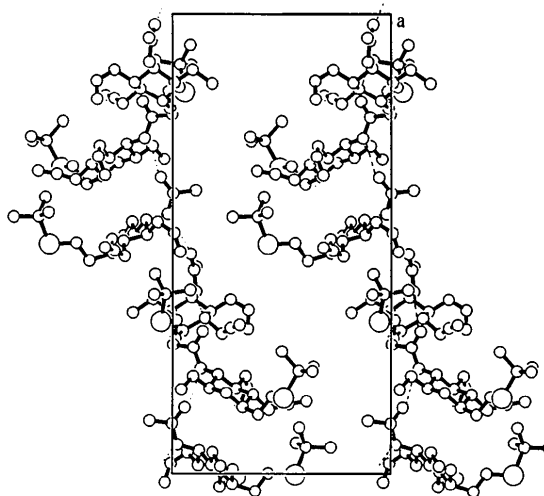


Fig. 2. Packing diagram showing the hydrogen bonds (O20...N18') forming the sixfold screw axis parallel to *c*. Phenyl groups have been omitted for clarity.

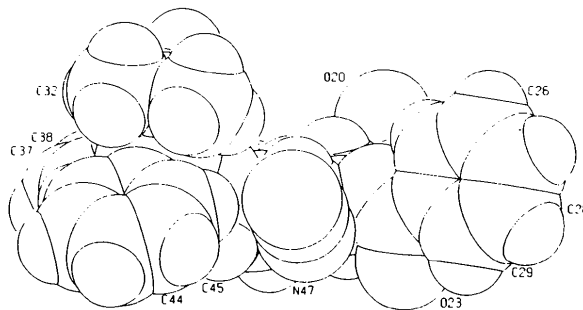


Fig. 3. Space-filling diagram looking from N49 towards C15, showing the cleft in the molecule.

The molecule showed no unusual interatomic distances or angles. Selected torsion angles are given in Table 2. The angles of mean planes relative to the plane of C1, C3, C5 are as follows: phenyl groups C12–C17 and C24–C29 18.8(2) and 70.4(2)°, respectively; acetamide group N18–C21 86.0(2)°. Significant independent thermal motion occurs in each of the side groups of the glucose moiety. Attempts to resolve the 'wagging' motion of the azide group as disorder were not successful. The *tert*-butyldiphenylsilyl group is positioned to minimize contacts with the rest of the molecule. The plane of the methyl C atoms (C32, C33 and C34) is only 14.9(3)° from being parallel to the plane of C1, C3 and C5. The phenyl groups at C35 and C41 are related by an approximate mirror plane through Si30, C31 and C32. There is no disorder and the thermal motion is largely libration of the whole *tert*-butyldiphenylsilyl group about an axis close to Si30–C31. This motion is absorbed by the O6–C6 bond, approximately parallel to Si30–C31 and not coupled to the glucose moiety.

The unusual space group, $P6_5$, occurs because of hydrogen bonding between acetamido groups. The molecules are connected into a spiral by interaction between O20 and H18–N18 of the molecule at $(1 + x - y, x, z - \frac{1}{6})$ [2.755(5) Å, Fig. 2]. The molecule has a cleft running across the glucose, on the face adjacent to the *tert*-butyl group, from C15 towards N49 (Fig. 3). This prevents other short intermolecular contacts which would occur from the action of the sixfold screw axis.

Experimental

Crystals of the title compound were grown from an ethyl acetate solution.

Crystal data

$C_{38}H_{42}N_4O_6Si$
 $M_r = 678.85$
 Hexagonal
 $P6_5$
 $a = 15.2730(10)$ Å
 $c = 27.399(3)$ Å
 $V = 5535.0(8)$ Å³
 $Z = 6$
 $D_x = 1.222$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 250 reflections
 $\theta = 2-22^\circ$ which occurred in 2 regions 90° apart and 5° wide at $\kappa = 0$
 $\mu = 0.113$ mm⁻¹
 $T = 293(2)$ K
 Block
 $0.6 \times 0.4 \times 0.25$ mm
 Colourless

Data collection

Enraf–Nonius CAD-4 FAST diffractometer
 Area detector
 Absorption correction: none
 18 978 measured reflections
 5421 independent reflections

3333 observed reflections [$I > 2\sigma(I)$]
 $R_{int} = 0.0914$
 $\theta_{max} = 25.09^\circ$
 $h = -9 \rightarrow 16$
 $k = -16 \rightarrow 14$
 $l = -22 \rightarrow 29$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0400$
 $wR(F^2) = 0.0919$
 $S = 0.635$
 5420 reflections
 450 parameters
 H atoms were refined using a riding model, refining U_{iso} in groups

$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.058$
 $\Delta\rho_{max} = 0.193$ e Å⁻³
 $\Delta\rho_{min} = -0.171$ e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$			
	x	y	z	U_{eq}
C1	0.8320 (3)	0.8224 (3)	-0.0194 (1)	0.0399 (9)
O1	0.9069 (2)	0.8163 (2)	-0.0458 (1)	0.0517 (7)
C2	0.7924 (3)	0.8789 (3)	-0.0498 (1)	0.0368 (8)
C3	0.7113 (3)	0.8824 (2)	-0.0186 (1)	0.0338 (8)
O3	0.6668 (2)	0.9313 (2)	-0.0454 (1)	0.0381 (5)
C4	0.6308 (2)	0.7772 (2)	-0.0048 (1)	0.0352 (8)
C5	0.6797 (3)	0.7254 (3)	0.0223 (1)	0.0397 (8)
O5	0.7541 (2)	0.7238 (2)	-0.0087 (1)	0.0418 (6)
C6	0.6079 (3)	0.6196 (3)	0.0386 (1)	0.0458 (9)
O6	0.5440 (2)	0.5605 (2)	-0.0003 (1)	0.0473 (6)
C11	0.9601 (3)	0.7795 (4)	-0.0165 (1)	0.0582 (12)
C12	1.0689 (3)	0.8300 (3)	-0.0319 (1)	0.0433 (9)
C13	1.1178 (3)	0.7752 (3)	-0.0323 (1)	0.0455 (9)
C14	1.2192 (3)	0.8204 (4)	-0.0443 (1)	0.0616 (11)
C15	1.2725 (4)	0.9201 (4)	-0.0556 (2)	0.0711 (13)
C16	1.2258 (4)	0.9761 (3)	-0.0546 (2)	0.0747 (14)
C17	1.1241 (4)	0.9312 (3)	-0.0433 (1)	0.0609 (11)
N18	0.8722 (2)	0.9776 (2)	-0.0628 (1)	0.0388 (7)
C19	0.9056 (4)	1.0019 (3)	-0.1085 (2)	0.0594 (12)
O20	0.8639 (3)	0.9451 (2)	-0.1431 (1)	0.0836 (11)
C21	0.9973 (5)	1.1044 (4)	-0.1147 (2)	0.096 (2)
C22	0.6609 (3)	1.0069 (2)	-0.0222 (2)	0.0381 (8)
O23	0.6904 (2)	1.0338 (2)	0.0187 (1)	0.0550 (7)
C24	0.6142 (3)	1.0513 (2)	-0.0532 (1)	0.0405 (9)
C25	0.5964 (3)	1.0302 (3)	-0.1022 (2)	0.0558 (11)
C26	0.5593 (4)	1.0813 (4)	-0.1297 (2)	0.0748 (14)
C27	0.5404 (3)	1.1515 (3)	-0.1071 (2)	0.0685 (13)
C28	0.5556 (3)	1.1703 (3)	-0.0590 (2)	0.0625 (12)
C29	0.5929 (3)	1.1209 (3)	-0.0319 (2)	0.0540 (10)
Si30	0.49074 (7)	0.43650 (7)	0.00251 (3)	0.0385 (2)
C31	0.4225 (3)	0.3885 (3)	-0.0573 (1)	0.0491 (9)
C32	0.3583 (3)	0.2735 (3)	-0.0564 (2)	0.0582 (11)
C33	0.4994 (4)	0.4187 (4)	-0.0995 (1)	0.0753 (14)
C34	0.3537 (4)	0.4331 (4)	-0.0660 (2)	0.095 (2)
C35	0.5958 (2)	0.4096 (2)	0.0117 (1)	0.0357 (8)
C36	0.5986 (3)	0.3441 (3)	0.0452 (1)	0.0626 (12)
C37	0.6828 (4)	0.3329 (4)	0.0506 (2)	0.0700 (13)
C38	0.7656 (4)	0.3863 (4)	0.0233 (2)	0.0686 (12)
C39	0.7659 (3)	0.4532 (4)	-0.0096 (2)	0.0794 (14)
C40	0.6841 (3)	0.4654 (3)	-0.0151 (2)	0.0592 (11)
C41	0.3986 (3)	0.3934 (3)	0.0544 (1)	0.0487 (10)
C42	0.3686 (4)	0.3068 (4)	0.0829 (2)	0.0756 (14)
C43	0.2968 (4)	0.2811 (5)	0.1203 (2)	0.105 (2)
C44	0.2552 (4)	0.3439 (7)	0.1279 (2)	0.107 (3)
C45	0.2822 (5)	0.4241 (6)	0.1009 (3)	0.112 (2)
C46	0.3537 (3)	0.4497 (4)	0.0659 (2)	0.0807 (15)
N47	0.5572 (2)	0.7827 (2)	0.0285 (1)	0.0446 (8)
N48	0.4700 (3)	0.7349 (3)	0.0164 (1)	0.0636 (10)
N49	0.3856 (4)	0.6910 (5)	0.0097 (2)	0.120 (2)

Table 2. Selected geometric parameters (Å, °)

C1–O1	1.395 (4)	C5–O5	1.429 (4)
C1–O5	1.406 (4)	C5–C6	1.498 (5)
C1–C2	1.526 (4)	C6–O6	1.423 (4)

O1—C11	1.440 (4)	O6—Si30	1.647 (2)
C2—N18	1.430 (4)	N18—C19	1.333 (5)
C2—C3	1.528 (5)	C19—O20	1.226 (5)
C3—O3	1.438 (4)	C19—C21	1.499 (7)
C3—C4	1.504 (5)	C22—O23	1.200 (4)
O3—C22	1.361 (4)	C22—C24	1.475 (5)
C4—N47	1.481 (4)	N47—N48	1.202 (5)
C4—C5	1.524 (5)	N48—N49	1.132 (5)
O1—C1—O5	108.7 (3)	O5—C5—C4	108.6 (3)
O1—C1—C2	109.0 (3)	C6—C5—C4	114.9 (3)
O5—C1—C2	110.9 (3)	C1—O5—C5	111.1 (2)
C1—O1—C11	112.3 (2)	O6—C6—C5	111.1 (3)
N18—C2—C1	111.2 (3)	C6—O6—Si30	118.8 (2)
N18—C2—C3	112.4 (3)	C19—N18—C2	122.3 (3)
C1—C2—C3	105.8 (3)	O20—C19—N18	122.5 (4)
O3—C3—C4	109.7 (3)	O20—C19—C21	122.3 (4)
O3—C3—C2	109.5 (3)	N18—C19—C21	115.2 (4)
C4—C3—C2	110.3 (3)	O23—C22—O3	123.7 (3)
C22—O3—C3	116.7 (3)	O23—C22—C24	124.4 (3)
N47—C4—C3	109.4 (2)	O3—C22—C24	111.9 (3)
N47—C4—C5	108.2 (3)	N48—N47—C4	116.0 (3)
C3—C4—C5	109.0 (3)	N49—N48—N47	173.2 (4)
O5—C5—C6	108.6 (3)		
C3—C4—N47—N48	126.1 (3)	O3—C3—C4—N47	-63.5 (3)
C5—C6—O6—Si30	157.6 (2)	O1—C1—C2—N18	-57.6 (4)
C1—O1—C11—C12	-145.4 (3)	C6—C5—C4—N47	60.8 (4)
C3—O3—C22—O23	-0.0 (5)		

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Conformational Studies of *trans*-1,4-Substituted Cyclohexanes. I. *trans*-1,4-Cyclohexanedicarbonitrile

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Abstract

The molecules of the title compound (C₈H₁₀N₂), which each adopt a chair conformation with the CN substituents equatorially bonded, lie on crystallographic inversion centres and are linked by CN···CN intermolecular interactions to form (101) sheets. The sheets are additionally stabilized by short C—H···N contacts.

Comment

The molecules of *trans*-1,4-cyclohexanedicarboxylic acid and its derivatives exhibit, in solution, a non-vanishing dipole moment (Barón, 1991, and references therein). Similar results observed in other 1,4-disubstituted cyclohexanes, *e.g.* 1,4-cyclohexanedione and 1,4-bis(dicyanomethylene)cyclohexane, have been described in terms of an equilibrium between chair and flexible forms (Le Févre & Le Févre, 1956) or as due to a predominance of a deformed conformation in solution (Aihara, Kitazawa & Iwasaki, 1968; Barón, 1991). Low-temperature X-ray single-crystal data have shown that the molecules of 1,4-

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After preliminary photographs, the unit cell was refined and data collected by the SERC Diffractometer Service (Cardiff University). The enantiomer and, thus, the space group were chosen on chemical grounds, and confirmed by the Flack (1983) parameter of $-0.09(15)$. Crystal decay was monitored by comparing intensities of common or symmetry-related reflections as these occurred on different exposures of the area detector during data collection. No significant decay was observed.

Data collection: *MADNESS* (Enraf–Nonius, 1990). Cell refinement: *MADNESS*. Data reduction: *MADNESS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTON92* (Spek, 1992a); *PLATON92* (Spek, 1992b).

The SERC Diffractometer Service are thanked for the collection of X-ray data, and SERC/DTI (in conjunction with Celltech, Glaxo, ICI and The Wellcome Foundation) for support.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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